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Immobilization of Lanthanide Oxides Waste from Pyrochemical Process

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Abstract

Lanthanide radioactive wastes are generated during the LiCl-KCl waste salt purification process developed in KAERI. The phosphate-based ceramics were studied for the immobilization of the wastes. The immobilization matrix developed in this study (ZIT ceramic wasteform) composed of zinc titanate (Zn_2TiO_4), CaHPO_4 , SiO_2 and B_2O_3 . The lanthanide oxides were reacted with CaHPO_4 during solid phase sintering. The reaction products of lanthanides phosphate (LnPO_4), which have a composition similar to monazite, has been developed as a high-level nuclear waste host. The physico-chemical properties (XRD, SEM, density and thermal conductivity) and leach resistance of the borosilicate glass and ZIT wasteforms are discussed in this paper.

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Key words: Pyrochemical; lanthanide; immobilization; borosilicate glass; KAERI

1. Introduction

Pyro-processing is a technology by which effective ingredients such as uranium contained in spent nuclear fuel from nuclear power plants may be recovered and recycled as fuel in fast reactors. Fast reactors are the next generation nuclear reactors, which significantly improve uranium utilization and greatly reduce the amount, toxicity, and calorific power of high level radioactive wastes. Radioactive lanthanide (Ln) oxide waste in powder form is produced from residuals of the LiCl-KCl waste salt purification process developed in KAERI [1-3]. The radioactive oxide powder of the lanthanide fission products must be immobilized to a chemically stable solid waste form for long-term storage in a geological environment. A waste form is prepared by a vitrification method commercially applied for treatment of high-level waste, including melting/decomposing borosilicate glass medium with a waste to be solidified (slurry generated during the wet process) at about 1400 - 1500°C in an induction furnace, pouring the melt into a solidification drum, and subjecting it to a heat treatment to prevent cracking. There are many difficulties in maintenance of the equipment and lot of waste is produced due to problems such as control of internal compositions for high frequency

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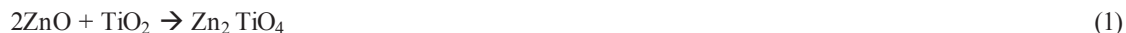
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induction, maintenance and replacement of internal structural materials necessitated by corrosion, presence of complicated elements, and condensation of highly volatile nuclides due to high temperatures during the process. Since the rare earth (RE) oxide in glass melt has a high tendency to make the glass crystalline which gets precipitated at the bottom of the melt, it is difficult to prepare a homogeneous glass waste form. Solid phase sintering is an alternative process being studied in KAERI, appears to be more advantageous than the melting process. The sintering process requires a lower processing temperature (about 1100°C), implying less demanding conditions for the process equipment and minimizing vaporization of the volatile compounds of some radio nuclides.

The present work reports the manufacture of Ln oxides wasteforms by solid phase sintering of a borosilicate glass (R7T7 glass, composition: Al_2O_3 5.8, SiO_2 54.3, B_2O_3 16.7, Na_2O 11.8, CaO 4.8, Li_2O 2.4, and ZrO_2 1.2 wt%) and the zinc titanate based ceramic (ZIT ceramic) matrix (composition: Zn_2TiO_4 60, CaHPO_4 17.5, SiO_2 10 and B_2O_3 12.5 wt%). The physico-chemical properties (XRD, SEM, density and thermal conductivity) and leach resistance [4] of the waste forms were determined which are discussed.

2. Experimental

Commercially available rare earth compounds, Nd_2O_3 , CeO_2 , Y_2O_3 , and La_2O_3 were used as surrogates of the oxides of lanthanide fission products. Zn_2TiO_4 powder was prepared using a conventional solid-state reaction method according to following reaction:



Stoichiometric mixture of starting materials was homogenized by ball milling using alumina media and calcined at 950°C for 4 hr. For CaHPO_4 synthesis, $\text{Ca}(\text{OH})_2$ was dissolved in water and then added to phosphoric acid, the reaction being:



After one day of magnetic stirring, the final precipitate was filtered and washed with deionized water and then dried at 100°C overnight. The reaction products were analyzed by X-ray powder diffraction (XRD, Rikaku, $\text{CuK}\alpha$ radiation).

In the direct vitrification of Ln oxides, a solidified waste form containing 20 wt% of Ln oxides was obtained by mixing with glass frit or ZIT matrix and heat treating at 1100°C for 4 hours by using an electrically heated resistance furnace and cooling down to room temperature in the furnace.

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized Zn_2TiO_4 and starting materials, $2\text{ZnO} + \text{TiO}_2$ mixture. It can be seen that the product pattern contains the peaks due to Zn_2TiO_4 and not those of starting materials. Fig. 2 shows the XRD patterns of the synthesized CaHPO_4 . It can be seen that the XRD peaks of the CaHPO_4 are present in the pattern.

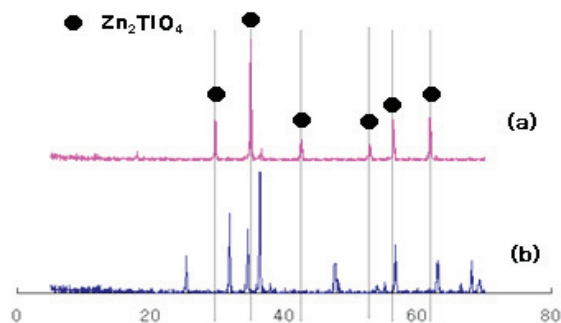


Fig. 1. XRD patterns: (a) Zn_2TiO_4 and (b) $2\text{ZnO} + \text{TiO}_2$.

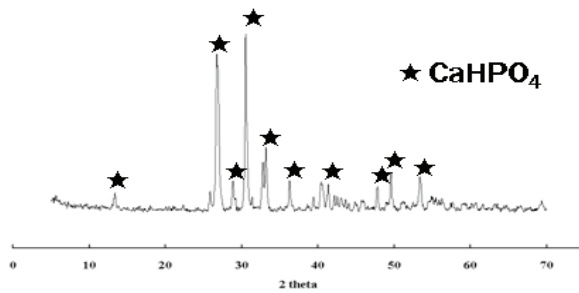
Fig.2. XRD pattern of CaHPO_4

Fig. 3 shows the microstructure of ZIT ceramic and borosilicate wasteforms. The SEM micrograph of ZIT wasteform indicates densified structure. But borosilicate waste form contains about 20 microns of hexagonal crystalline phase. The hexagonal crystalline phase was determined to be oxy-apatite $[\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2]$ by EDS and XRD analysis (Fig. 4). The components (Si and Ca) of the glass binder were consumed to form the crystal phase which weakened the binding effect. Fig. 4 shows the XRD patterns of borosilicate glass and ZIT ceramic wasteforms. The major phases of borosilicate glass and

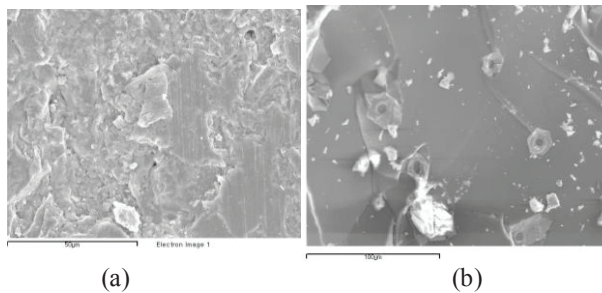


Fig. 3 Scanning electron micrographs of wasteforms: (a) ZIT ceramic and (b) borosilicate glass (R7T7).

ZIT wasteforms are oxy-apatite and monazite, respectively. Therefore, it is obvious that Ln oxides react with CaHPO_4 and produce the stable Ln-monazite during sintering process.

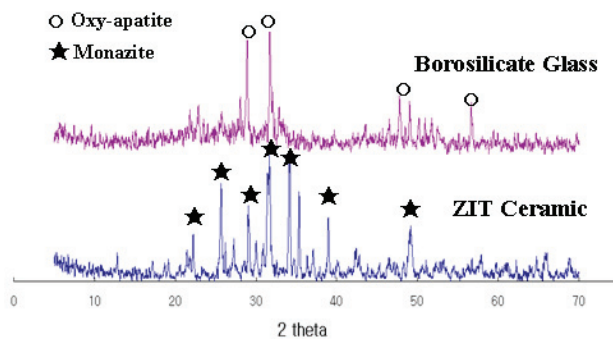


Fig. 4. XRD patterns of wasteforms.

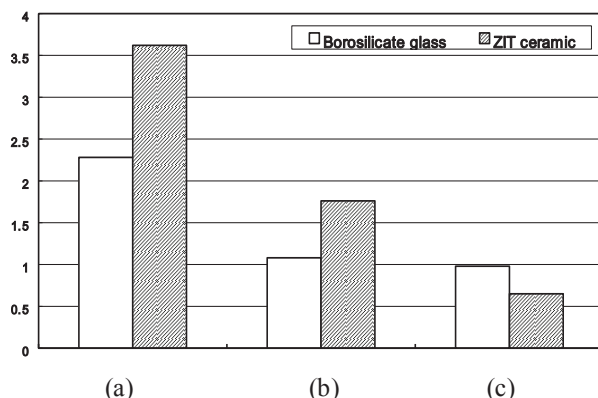


Fig. 5. Physical properties of wasteforms; (a) density (g/cm^3), (b) thermal conductivity (W/mK) and (c) specific heat (J/gK).

Fig. 5 shows the physical properties of wasteforms. The density of the borosilicate glass wasteform has a lower density (2.3 g/cm^3) than that of ZIT ceramic wasteform (3.7 g/cm^3). The thermal conductivity and specific heat, of the ZIT ceramic waste form are higher than borosilicate glass wasteform.

Fig. 6 shows the leach rate of elements of the PCT-A leaching test. The leach rates of the Ln elements were below $10^{-5} \text{ g/m}^2\text{day}$ and the components of the glass were about $10^{-3} \sim 10^{-1} \text{ g/m}^2\text{day}$. Using monazite for immobilization of Ln elements, it is possible to increase the waste loading above 20 wt% and obtain a highly monolithic waste form [5-9].

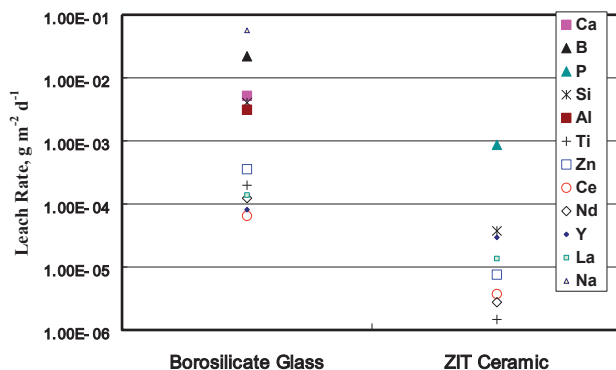


Fig. 6. Leach rate of wasteforms according to PCT-A.

4. Conclusion

For fabricating a monolithic waste form containing Ln oxides, vitrification at high temperature or a ceramization by a HIP method has to be used. In this study, a ZIT ceramic waste form was successfully produced at a mild condition, where the structure of the wasteform was almost equivalent to the product by a high temperature process. The waste form is highly resistant to leaching process.

Acknowledgement

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